SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF ELLIPSOIDAL La₂O₂SO₄:Eu³⁺ PHOSPHORS

SINTEZA IN FOTOLUMINESCENČNE LASTNOSTI ELIPSOIDALNIH La₂O2_SO₄:FLUORESCENTOV Eu³⁺

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This research was focused on the homogeneous precipitation synthesis of a series of Eu^{3+} ion-activated ellipsoidal $La_2O_2SO_4$ phosphors based on the $La_2(SO_4)_3$ -CO(NH₂)₂ reaction system. The structural identification, thermal analysis, morphology and luminescence properties of the as-prepared products were characterized with Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry and differential scanning calorimetry (TG/DSC), field emission scanning electron microscopy (FESEM) and photoluminescence (PL) spectra. Pure $La_2O_2SO_4$ ellipsoidal particles with a long radius of about $2 \mu m$ and a short radius of about 1 μm were successfully prepared by calcining a rhombus-like precursor at 800 °C for 2 h in air. The formation mechanism of the precursor and its corresponding calcination product were also proposed. Photoluminescence results revealed that the strongest red emission peak was centered at 619 nm upon 249-nm ultraviolet (UV) light excitation in $La_2O_2SO_4:x\%Eu^{3+}$ (x = 3, 6, 9, 12 and 15) phosphors. The exchange interaction was responsible for the concentration quenching mechanism of the ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in the $La_2O_2SO_4$ host lattice. The optimal x value was 15 and the corresponding decay process showed a single exponential decay behavior whose lifetime τ and color correlation temperature (CCT) were calculated to be 2.112 ms and 2752 K, respectively.

Keywords: lanthanium oxysulfate, ellipsoidal morphology, homogeneous precipitation reaction, photoluminescence

V raziskavi o homogeni precipitacijski reakcijski sintezi so aktivirali vrsto ionov Eu^{3+} v fluorescentu $La_2O_2SO_4$ oziroma materialu, ki ima fotoluminescenčne lastnosti. Uporabljeni reakcijski sistem je temeljil na kombinaciji spojin $La_2(SO_4)_3$ in $CO(NH_2)_2$. Strukturno identifikacijo so izvedli s pomočjo termične in morfološke analize. Luminescenčne lastnosti pripravljenih izdelkov so označili s Fourierjevo transformacijsko infrardečo spektroskopijo (FTIR) in fotoluminescenčno spektroskopijo (PL). Morfološko in fizikalno-kemijsko karakterizacijo pa so izvedli s pomočjo vrstične elektronske mikroskopije na osnovi emisije polja (FESEM), rentgenske difrakcije (XRD), termogravimetrije (TG) in diferencialne vrstične kalorimetrije (DSC). S kalcinacijo romboedričnega prekurzorja pri njegovem zadrževanju dve uri na 800 °C v zračni atmosferi so uspešno pripravili elipsoidalne delce $La_2O_2SO_4$ z vzdolžnim polmerom približno 2 µm in prečnim polmerom približno 1 µm. Na osnovi analiz so predlagali mehanizem tvorbe in nastanka kalcinacijskega produkta. Rezultati analiz fotoluminescence so odkrili, da se najmočnejši emisijski vrh v rdeči svetlobi nahaja na 619 nm pri 249 nm vzbujanju ultravijolične svetlobe v fluorescentu z razmerjem $La_2O_2SO_4$: x/% Eu^{3+} (x = 3, 6, 9, 12 in 15). Izmenjalna interakcija je bila odgovorna za tako imenovani koncentracijsko zamrznitveni mehanizem ${}^{5}Do \rightarrow {}^{7}F_2$ prehod ionov Eu^{3+} v rešetki gostiteljice ($La_2O_2SO_4$). Ugotovljena optimalna vrednost x/% je bila 15 in odgovorjajoči proces razpada je pokazal singularno eksponencialno obnašanje, katerega izračunana doba trajanja τ je bila 2,112 ms pri barvni korelacijski temperaturi (CCT) 2752 K.

Ključne besede: lantanov oksisulfat, elipsoidalna morfologija, reakcija homogene precipitacije, fotoluminescenca

1 INTRODUCTION

In the past decades, rare-earth (RE) ion-doped phosphors received considerable attention due to their special luminescent properties based on the unique intra 4*f* transitions of trivalent RE ions.¹ Because of this, rare-earth phosphor materials became a research highlight and some phosphors have recently been successfully applied in various fields, such as fluorescent lamps, white light-emitting diodes (WLEDs), X-ray intensifying screen, X-ray computed tomography (X-CT), biological labels, and so forth. As is known to us, the RE phosphor family involves numerous stable host matrixes, such as oxides, sulfides, oxysulfides, oxysulfates, fluorides, phosphates, molybdates, etc. Among these compounds,

lanthanide oxysulfates (Ln₂O₂SO₄) activated by various trivalent RE ions (Eu³⁺, Tb³⁺, Pr³⁺, Ce³⁺, Yb³⁺, Er³⁺ and so on) have attracted considerable attention because of their unique luminescence behavior, sharp emission peaks, high quantum yields, low phonon energy and low toxicity; they have been widely applied in bioimaging, optical temperature sensors, medical surgery and so on. Lanthanium oxysulfate (La₂O₂SO₄) is one of the most important lanthanide oxysulfate matrix materials.² and it has attracted increasing attention in recent years due to its high oxygen-storage capacities, good thermal stability, as well as enhanced catalyst activity;³⁻⁵ it can provide potential applications in the fields including large-volume oxygen-storage materials,6 auxiliary sensing electrodes,⁷ solid electrolytes⁸ and catalysts for the water-gas shift reaction.9

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So far, various synthetic routes have been explored to prepare lanthanide oxysulfate (Ln₂O₂SO₄) materials, including the solid-state reaction method^{10,} thermal decomposition method,^{11,12} sulfide oxidation method,⁸ co-precipitation method¹, hydrothermal synthesis,¹³ template method,¹⁴ molten salt synthesis¹⁵ and so on. However, the main three methods are high temperature, time-consuming preparation process and the release of sulfur oxide gas (SO₂ or SO₃), which is harmful to the environment. The obtained La₂O₂SO₄ compounds are bulk materials with an irregular morphology. Moreover, the morphology of the obtained powder needs to be improved with the co-precipitation method. In recent years, some researchers have prepared a series of high-yield and uniform RE₂O₂SO₄ hollow spheres with the hydrothermal method using L-cysteine as the biomolecular template and polyvinylpyrrolidone (PVP) as the surfactant.16 The study by Mei Yang showed that the three-dimensional (3D) nanofibrous structures of La₂O₂SO⁴:Eu³⁺ would provide multifunctional applications, such as optical displays, biological labels and bio-imaging.¹⁷ However, the procedures involved in these routes are complicated, and it is generally difficult to carry out mass production.

To the best of our knowledge, so far less work has been done on the preparation of ellipsoidal La₂O₂SO₄:Eu³⁺ phosphors. So, it is still challenging and imperative to exploit an efficient but simple way for the synthesis of ellipsoidal La₂O₂SO₄:Eu³⁺ phosphors. Herein, we thus put forward a homogeneous precipitation reaction to synthesize La₂O₂SO₄:Eu³⁺ phosphor using commercial lanthanum sulfate octahydrate $(La_2(SO_4)_3 \cdot 8H_2O)$, europium nitrate hexahydrate $(Eu(NO_3)_3 \cdot 6H_2O)$ and urea $(CO(NH_2)_2)$ as the starting materials where a structural analysis (FTIR and XRD), thermal analysis, morphology and photoluminescence of the obtained products are characterized and discussed in detail. This homogeneous precipitation method has the characteristics of a simple inexpensive process, easy to use in mass production and environment-friendly. The simplicity of this synthetic approach makes it promising also for the preparation of other RE-activated phosphors.

2 EXPERIMENTAL PART

In this study, $La_2(SO_4)_3 \cdot 8H_2O$ (a purity of 99.99 %), Eu(NO₃)₃·6H₂O (a purity of 99.99 %) and urea (CO(NH₂)₂, AR) were used as the starting materials without any further purification. Among them, $La_2(SO_4)_3 \cdot 8H_2O$ and Eu(NO₃)₃·6H₂O were received from Jining Tianyi New Material Co. Ltd, China. Urea was purchased from Sinopharm Chemical Reagent Co. Ltd, China. First of all, a stoichiometric amount of $La_2(SO_4)_3 \cdot 8H_2O$ was dissolved in ultrapure water with a resistivity of 18 MQ·cm and a 0.05-M La₂(SO₄)₃ solution was obtained. Secondly, the La₂(SO₄)₃ solution with a volume of 250 mL was transferred to a 500-mL beaker. During continuous stirring, urea was added into the beaker in a molar ratio of La³⁺: urea = 1 : 25. Then the beaker was sealed with a plastic wrap and heated in a water bath kettle at 90 °C for 2 h. After naturally cooling down to room temperature, the sample was collected while cleaning it with deionized water and absolute ethanol for several times and then dried at 50 °C for 12 h to obtain the precursor. Thirdly, the precursor was calcined at 800 °C for 2 h to obtain a La₂O₂SO₄ sample. Finally, a series of Eu³⁺ doped La₂O₂SO₄ products were also prepared using the above methods. Here, the concentration of Eu³⁺ (*x*) in La₂O₂SO₄:*x*/%Eu³⁺ was (3, 6, 9, 12 and 15) %, respectively.

The phase structures were identified by a D8 Ad-X-ray diffractometer operating vance with $CuK_{\alpha} = 0.15406$ nm. FTIR spectra were obtained using an Agilent Cary 660 FTIR spectrophotometer using the KBr method. DSC/TG/DTG were performed using simultaneously a differential thermal analysis and thermogravimetry (SDT 2960). The particle morphologies of the products were observed with a Hitachi SU8000 field emission scanning electron microscope. PL spectra and a decay curve were recorded on a JASCO FP-8600 fluorescence spectrophotometer equipped with the ISF-834 phosphorescence lifetime measurement system. CIE coordinates were calculated from the PL emission spectra data based on the 1931 CIE standard for colorimetry.

3 RESULTS AND DISCUSSION

3.1 Feasibility analysis of preparing a target product

In this study, the selection of $La_2(SO_4)_3$ as the raw material has a dual function of providing rare-earth cations and anion groups. Here, the hydrolyzation process of La₂(SO₄)₃ can provide La³⁺ ions and liberate SO₄²⁻ groups. Moreover, urea is a weak Brönsted base and its aqueous solution can release CO₃²⁻ and OH⁻ groups at a temperature of 90 °C for 2 h. In the La₂(SO₄)₃⁻ urea system, SO₄²⁻, CO₃²⁻ and OH⁻ groups are hard bases and the hardness has the following order: $SO_4^{2-} > CO_3^{2-} > OH^-$, La³⁺ ions are hard acids. According to hard-soft acid-base (HSAB) principle, hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases.¹⁸ So, the above La³⁺ ions and functional groups are easily combined with each other to form a precursor containing lanthanum hydroxyl, carbonate and sulfate, which can form the target product (La₂O₂SO₄) through dehydroxylation and decomposition of carbonate at a high temperature.

3.2 Structural transformation of the precursor

In order to qualitatively determine the structural information of the precursor, a FTIR analysis was carried out, as shown in **Figure 1**. Evidence of the presence of hydroxyl (OH⁻), carbonate (CO_3^{2-}) and sulfate (SO_4^{2-}) groups in the precursor can be obtained with FTIR spectroscopy (**Figure 1a**). The spectrum shows the absorp-

tion splitting peaks of physically absorbed water, crystal water, hydroxyl groups (near 3453 cm⁻¹ and 1630 cm⁻¹), the CO₃²⁻ groups (near 1463 cm⁻¹, 1375 cm⁻¹, 850 cm⁻¹ and 750 cm $^{-1})$ and the $SO_4{}^{2-}$ groups (near 1142 cm $^{-1},$ 1067 cm⁻¹, 656 cm⁻¹ and 588 cm⁻¹), indicating that the precursor is composed of lanthanum hydroxyl, carbonate and sulfate groups with some crystal water. After the precursor is calcined at 800 °C (Figure 1b), the broad absorption peak centered near 3453 cm⁻¹ becomes negligible, which is associated with the dehydroxylation of hydroxyl groups in the precursor. Moreover, a narrow absorption peak centered at about 3609 cm⁻¹ appears, the CO32- absorption peaks (near 1463 cm⁻¹ and 1375 cm⁻¹) become negligible, suggesting the decomposition of the CO₃²⁻ groups in the precursor. However, the weak vibration peak near 1480 cm⁻¹ shows that the product absorbed water and carbon dioxide (CO₂) from the air and then formed CO₃²⁻ groups. The SO₄²⁻ absorption peaks (near 1142 cm⁻¹, 1067 cm⁻¹, 656 cm⁻¹ and 588 cm⁻¹) split into some narrow peaks (near 1173 cm⁻¹, 1100 cm⁻¹, 1058 cm⁻¹, 990 cm⁻¹, 654 cm⁻¹, 616 cm⁻¹ and 592 cm⁻¹). The FTIR result shows that the SO₄²⁻ groups still exist in the calcined product and becomes a component of the target product.

The phase structure was investigated with XRD focusing on the precursor and its calcined product, as shown in **Figure 2**. It is obvious from **Figure 2a** that the precursor has a good crystalline structure with obvious diffraction peaks. However, the diffraction pattern of the precursor is inconsistent with the data reported in the JCPDS card database and the crystal structure is still unidentified, which may be attributed to the formation of a new phase containing La³⁺, OH⁻, CO₃²⁻ and SO₄²⁻ groups and some crystal water. This result is confirmed by the above FTIR spectroscopy. When the precursor is cal-



Figure1: FTIR spectra of: a) the precursor, b) La₂O₂SO₄

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Figure 2: XRD patterns: a) the precursor, b) $La_2O_2SO_4$ sample, c) JCPDS card of $La_2O_2SO_4$

cined at 800 °C, the precursor undergoes the following thermal decomposition reaction:

$$La_{2}(OH)_{2}CO_{3}SO_{4} \cdot mH_{2}O =$$

= $La_{2}O_{2}SO_{4} + CO_{2}\uparrow + (m+1)H_{2}O\uparrow$ (1)

Diffraction peaks of the pure $La_2O_2SO_4$ phase begin to appear in the XRD pattern (**Figure 2b**) and the obtained diffraction pattern is well consistent with the data reported in the JCPDS card No. 00-016-0501 (**Figure 2c**), further confirming the rationality of the above feasibility analysis and the formation of the target product ($La_2O_2SO_4$).

3.3 DSC-TG-DTG analysis of the precursor

To understand the decomposition behavior and determine the optimal calcination temperature for the precursor, DSC-TG-DTG of the precursor was conducted from room temperature to 1000 °C and the results are shown in **Figure 3**. The TG curve shows a continuous weight loss between room temperature and 1000 °C with an overall weight loss of approximately 37.19 w/%. The total weight loss mainly consists of the following steps over the whole temperature range, seen from the DTG curve. The weight loss in the temperature range from room temperature to ≈ 170 °C is about 8.96 w/%, which seems to be related mostly to the removal of physically adsorbed water from the precursor. This weight loss corresponds to a weak endothermic peak at around 129 °C in the DSC curve, and DTG maxima at about 123 °C in the DTG curve. The weight loss between ≈ 170 °C and \approx 473 °C is about 8.53 w/%; there are no obvious endothermic peak in the DSC curve and no extreme value in the DTG curve, which is related to the removal of crystal water. The weight loss in the temperature range from ≈ 473 °C to ≈ 639 °C is about 13.49 w/%, which is associated with the complete dehydroxylation of the precursor with a weak endothermic peak at ≈ 591 °C in the DSC curve. The maximum value on DTG curve also appears near 591 °C. The last weight loss of about 6.21 w/% starting at \approx 639 °C is associated with the complete decomposition of the CO₃²⁻ groups of the precursor. At the same time, this weight loss is accompanied with a weak endothermic peak at around 763 °C in the DSC curve and a broad peak centered at about 763 °C in the DTG curve. Moreover, as shown in Figure 3, little weight changes can be observed at temperatures greater than 800 °C on the TG curve, indicating that at temperatures higher than 800 °C the thermal decomposition is basically finished in the present study. These results are consistent with those obtained with the XRD analysis and FTIR spectra.

3.4 FESEM morphological analysis

The morphologies of the precursor and its corresponding calcination product (800 °C, 2 h) were investigated with FESEM. **Figure 4a** shows a FESEM image of the precursor, indicating that the precursor is rhombus-shaped with the edge lengths ranging from $0.5-1 \mu m$ and a thickness about 100 nm. In addition, the obtained particles showed a smooth surface and a good crystal habit. This formation mechanism may be related to the supersaturation degree of crystallographic ions. In the La₂(SO₄)₃-CO(NH₂)₂ homogeneous reaction system, the



Figure 3: DSC-TG-DTG curves of the precursor

molar ratios of La₂(SO₄)₃ and CO(NH₂)₂ are relatively small (m = 25), making the concentration of crystallographic ions lower and leading to a lower supersaturation. According to the Gibbs-Thomson formula of the classical nucleation theory Equation (2) is formed as follows:¹⁹

$$J = A \exp[B(\ln S)^{-2}]$$
(2)

where J and S are the nucleation rate and supersaturation, A and B are the constants. Therefore, nucleation rate J of the current reaction system is low. Accordingly, the nucleus growth is dominated by attachment kinetics, and a free growth of crystal faces takes place, resulting



Figure 4: FE-SEM images: a) the precursor, b) La₂O₂SO₄ sample, c) an enlarged photograph of (b)

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in the formation of rhombus-like crystals related to their inherent crystal structure. Figure 4b shows a FESEM image of La₂O₂SO₄. Compared with Figure 4a, it can be seen from Figure 4b that the La₂O₂SO₄ particle morphology changed significantly. These particles are seriously agglomerated and no longer have smooth surfaces or a regular shape. In order to clearly observe the internal structure of the particles, Figure 4c shows a highermagnification FESEM image of La₂O₂SO₄. The obtained La₂O₂SO₄ particles possess an ellipsoidal shape with a long radius of about 2 µm and a short radius of about 1 µm. Moreover, the ellipsoidal surface is mainly composed of quasi-spherical small particles with a size of less than 100 nm. The above investigation might be explained as follows. During the calcination of the precursor, rhombus-like crystals were destroyed due to a high temperature and ellipsoidal particles were found. At the same time, the water vapor and carbon dioxide were generated during the calcination of the precursor. These gases generated a great pressure inside the precursor, promoting the decomposition of rhombic crystals into nanoparticles.

3.5 Photoluminescence analysis

Figure 5 shows the PL excitation and emission spectra of La₂O₂SO₄:x/%Eu³⁺ (x = 3, 6, 9, 12 and 15) phosphors. From Figure 5, we can see that the contour lines of all the PL excitation and emission spectra of $La_2O_2SO_4:x/\%Eu^{3+}$ (x = 3, 6, 9, 12 and 15) phosphors are similar and the PL intensity of the excitation and emission spectra is maximum when the doping concentration Eu³⁺ of is 15 x/%. As a representative, La₂O₂SO₄:15%Eu³⁺ phosphor was selected for the excitation and emission spectra analysis. The excitation spectrum was recorded by monitoring the emission wavelength of 619 nm. As can be seen in Figure 5a, two broad absorption peaks located at approximately 249 nm and 305 nm are observed: they can be attributed to the change-transfer transitions of O2--Eu3+ and SO42--Eu3+, respectively. The other characteristic absorption peaks can be ascribed to the *f*-*f* transitions of Eu^{3+} ions at (363, 380, 395, 414, 464 and 465) nm in the longer wavelength region. These characteristic absorption peaks for the electron transition of Eu³⁺ ions in the excitation spectrum can be similar to those of the Eu³⁺ doped La₂O₂SO₄ materials achieved with other synthetic routes.¹⁵ As shown in Figure 5b, upon excitation at 249 nm, the emission spectrum of La₂O₂SO₄:15%Eu³⁺ phosphor consists of five emission peaks corresponding to the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 0, 1, 2, 3, 4) transitions of Eu^{3+} ions. It can be seen that the strongest red emission peak is centered at 619 nm, arising from the ${}^{5}D_{0} \rightarrow {}^{7}F2$ transition of Eu³⁺ ions. Other characteristic emission peaks in Figure 5b can be assigned to the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (581 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (596 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (651 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (701 nm) transitions of Eu³⁺ ions, respectively.



Figure 5: La₂O₂SO₄:x%Eu³⁺ (x= 3, 6, 9, 12, 15) phosphors: a) excitation spectra, b) emission spectra

the maximum doping concentration of For La₂O₂SO₄:x%Eu³⁺ phosphors, we prepared a series of Eu^{3+} doped $La_2O_2SO_4:x/\%Eu^{3+}$ phosphors. Figure 6 shows the curve of the influence of the concentration of Eu³⁺ ions on the luminescent intensity of La₂O₂SO₄:x/%Eu³⁺ phosphors and its corresponding log (I/C) and log (C) fitting curve. As shown in Figure 6a, the luminescent intensity is enhanced with the increasing Eu³⁺ ion concentration when the concentration of Eu³⁺ is less than or equal to 12 x/%; then it reaches its maximum value when 15 x/%. Therefore, it is reasonable to believe that the optimal concentration of Eu³⁺ can be determined to be 15 x/% in the present study.

In order to explore the concentration quenching mechanism, the relationship plot of the log(C) versus log(I/C) for the luminescent intensity of La₂O₂SO₄:x/%Eu³⁺ (x = 3, 6, 9, 12 and 15) phosphors at the 249 nm excitation and 619 nm emission wavelengths is shown in **Figure 6b**. According to Dexter's theory, the luminescence intensity is related to the doping concentration of the activator.²⁰ The concentration can be expressed with Equation (3):



Figure 6: a) Effects of different concentrations of Eu^{3+} ions on the emission intensity of $La_2O_2SO_4:x/\%Eu^{3+}$ phosphors and b) the relationship between log(I/C) and log(C) for $La_2O_2SO_4:x\%Eu^{3+}$ phosphors

$$\log (I/C) = (-s/d)\log C + \log f$$
(3)

where *d* is 3, *C* is the doping concentration and *f* is a constant independent of the doping concentration. When s = (3, 6, 8 and 10), the mechanism of concentration quenching is exchange interaction, electric dipole-electric dipole, electric dipole-electric quadrupole and electric quadrupole-electric quadrupole interaction, respectively.

By fitting the high concentration point in **Figure 6b**, the fitting curve with the R-square value of 0.99857 is:

$$\log(I/C) = 4.62334 - 0.77844 \log(C) \tag{4}$$

The slope parameter -s/d was determined to be -0.77844 (close to -1), yielding the corresponding value of 3 for *s*, and indicating that the mechanism of exchange interaction can be responsible for the concentration quenching effect of the ${}^{5}D_{0\rightarrow7}F_{2}$ transition of Eu³⁺ ions.

To figure out the emission color composition with different doping concentrations of Eu^{3+} , we employed the CIE chromaticity diagram to calculate the red emission and the results are shown in **Table 1** and **Figure 7**. When

x/% increases from 3 x/% to 15 x/%, in **Table 1**, the CIE chromaticity coordinates are calculated to be (0.6239, 0.3415), (0.6313, 0.3539), (0.6372, 0.3476), (0.6399, 0.3441) and (0.6420, 0.3391), respectively, where the CIE coordinates of the five samples are observed in a very narrow red area. This result demonstrates that Eu³⁺ ion-doped La2O2SO4 phosphors exhibited good red light emission with excellent color saturation. Moreover, the color correlation temperature (CCT) was also calculated to characterize the color emission. The CCT data are summarized in **Table 1**. The CCT is determined with McCamy's empirical Equation (5):²¹

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31$$
(5)

where $n = (x - x_e)/(y - y_e)$ and the chromaticity epicenter coordinates (x_e, y_e) are (0.3320, 0.1858). Their CCT values for La₂O₂SO₄:x%Eu³⁺ (x = 3, 6, 9, 12 and 15) phosphors are 2787 K, 2 247 K, 2 452 K, 2 577 K and 2 752 K, respectively, belonging to the penetrating low CCT light luminescence, which can be useful in a white light emitting diode (WLED) device and other fields.

Table 1: CIE coordinates and CCT values for La₂O₂SO₄:x/%Eu³⁺ (x = 3, 6, 9, 12 and 15) phosphors

No.	Samples	CIE (x, y)	CCT (K)
1	La2O2SO4:3%Eu3+	(0.6239, 0.3415)	2 429
2	La2O2SO4:6%Eu3+	(0.6313, 0.3539)	2 247
3	La2O2SO4:9%Eu3+	(0.6372, 0.3476)	2 452
4	La2O2SO4:12%Eu3+	(0.6399, 0.3441)	2 577
5	La ₂ O ₂ SO ₄ :15%Eu ³⁺	(0.6420, 0.3391)	2 752

The luminescent decay process of the as-prepared $La_2O_2SO_4$:15%Eu³⁺ phosphor excited at 249 nm and



Figure 7: CIE chromaticity diagram of $La_2O_2SO_4:x/\%Eu^{3+}$ (x = 3, 6, 9, 12 and 15) phosphors



Figure 8: Decay curve of the $La_2O_2SO_4$:15%Eu³⁺ phosphor excited by ultraviolet light at 249 nm

monitored at 619 nm was measured and plotted in **Fig-ure 8**. The decay curve can be fitted into a single exponential function as shown in Equation (6):

$$I = I_0 + A\exp(-t/\tau) \tag{6}$$

where *I* and *I*₀ are the luminescence intensities when the time is determined as *t* and 0, respectively, *A* is the constant, *t* is the time and τ is the lifetime value. The single exponential fitting specific equation with a R-Square value of 0.98295 is shown in the inset of **Figure 8**. The corresponding value of τ for La₂O₂SO₄:15%Eu³⁺ phosphor is 2.112 ms.

4 CONCLUSIONS

Ellipsoidal La₂O₂SO₄:Eu³⁺ phosphors have been successfully obtained with a homogeneous precipitation reaction combined with a calcination based on the $Eu(NO_3)_3-CO(NH_2)_2$ $La_{2}(SO_{4})_{3}$ system, using $La_2(SO_4)_3$, $Eu(NO_3)_3$ and $CO(NH_2)_2$ as the starting materials. The as-prepared precursor is composed of rhombus-like particles and can be converted into ellipsoidal La2O2SO4 particles at 800 °C in air. Photoluminescence properties reveal that the 15%Eu³⁺ doped La₂O₂SO₄ phosphor possesses the highest red peak (619 nm) under 249-nm UV light excitation whose corresponding lifetime and color correlation temperature (CCT) are calculated to be 2.112 ms and 2 752 K. These results imply that Eu³⁺ doped La₂O₂SO₄ phosphors have potential applications in white light emitting diode (WLED) devices and other research fields, such as oxygen storage or red display devices. The homogeneous precipitation synthesis is also a convenient and feasible method for synthesizing other rare-earth oxysulfate materials.

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